

A NEW TECHNIQUE FOR HYDRATE THERMAL DIFFUSIVITY MEASUREMENTS¹

D. J. Turner², P. Kumar^{2,3}, and E. D. Sloan^{2,4}

¹ Paper presented at the Fifteenth Symposium on Thermophysical Properties, June 22-27, 2003, Boulder, Colorado, U.S.A.

² Center for Hydrate Research, Colorado School of Mines, Golden, Colorado 80401, U.S.A.

³ . Oil and Natural Gas Corporation of India

⁴ To whom correspondence should be addressed. E-mail: esloan@mines.edu

ABSTRACT

Thermal property measurements of hydrates in various sediment mixtures are necessary to describe heat transfer to surroundings during well boring and gas production. An apparatus for measuring thermal diffusivity in various mixtures of hydrates with sediment has been constructed. The apparatus uses a new method for determining thermal diffusivity that has advantages over the von Herzen and Maxwell probe method. The new experiment is simple and inexpensive to construct and appears to be much more accurate than the $\pm 30\%$ reported for the probe. Thermal diffusivity of ice has been measured to determine the accuracy of the technique to within $\pm 5\%$. The thermal diffusivity for pure methane hydrate at various temperatures is reported.

KEY WORDS: hydrate; ice; thermal conductivity; thermal diffusivity

1. INTRODUCTION

Hydrates are pervasive in the seafloor and permafrost regions of the world [1]. These natural hydrates are usually associated with a sediment substrate [2, 3].

Waite et al. [4] have performed thermal conductivity measurements on hydrate sediment mixtures and found a maximum in thermal conductivity within a range of pure sediment and pure hydrate compositions. They attributed this non-linearity to be caused by poor contact of high thermal diffusivity sediment grains and cementing properties of lower thermal conductivity hydrates.

Thermal conductivity is a component of thermal diffusivity along with the heat capacity and density of the medium; each of these components can vary with hydrate fraction.

Therefore it is expected that thermal diffusivity will have a maximum like thermal conductivity, but for a different hydrate fraction.

2. EXPERIMENTAL SETUP

An experiment was constructed to measure thermal diffusivity of solids. The experimental apparatus, shown in Fig. 1, consisted of an 8-inch long, 2-inch inner diameter stainless steel cell submerged in a cooling bath. The cell had three thermocouples, which penetrated to three different radii within the cell: the center, the wall, and midway between the center and wall. A fourth thermocouple was used to measure the bath temperature. A gas

inlet/outlet was located at the top of the cell, along with a filter and pressure transducer. A nickel-chromium heating wire (18 gauge, 1.384 Ohms/m) was located through the centerline of the cell. The heating wire was electrically insulated with a thin plastic tube coating. A 3amp, 13.8Vdc power supply was connected to the heating wire, which could supply ~4.7W of power through the wire.

As discussed in the following section on the thermal diffusivity equation derivation, this cell configuration provided all of the necessary parameters for measuring thermal diffusivity, α , namely R_1 and R_2 (the distance of the center and midway thermocouples from the cell centerline), T_1 and T_2 at the respective thermocouples, and $[\Delta T/\Delta t]_1$ and $[\Delta T/\Delta t]_2$ at the respective locations. Distances R_1 and R_2 were constant in the apparatus.

The center thermocouple could also be used to ensure that the temperature near the heat source was below the melting point. The wall thermocouple was used to indicate when the heat wave from the heating wire had reached the outer wall.

3. DERIVATION OF THE THERMAL DIFFUSIVITY EQUATION

The thermal diffusivity apparatus utilized the Navier-Stokes heat equation for cylindrical geometry applied to a heat wave, which propagates from a line source into an infinite medium [5]. If no generation occurs, such as hydrate formation or dissociation, if the heat is transferred symmetrically from the line source, if the loss of heat axially is negligible (such

as with a long cell), and if no viscous dissipation occurs from moving phases, the general form of the Navier-Stokes equation greatly simplifies to give equation 3.1:

$$\frac{\partial T}{\partial t} = \alpha \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) \right] \quad (3.1),$$

where T is temperature, t is time, α is thermal diffusivity, r is radial distance from the cylinder center, and z is cylinder depth.

Although Equation (3.1) has an analytical solution, an approximate solution is preferential to our experimental set-up. For small time steps, the change in temperature with time may be linearized in discrete stages:

$$\frac{\partial T}{\partial t} \approx \frac{\Delta T}{\Delta t} \equiv m \quad (3.2),$$

where m is a constant equal to the change in temperature over a small time increment.

Equation (3.2) permits us to cast Equation (3.1) into the form of an ordinary differential equation. Thermal diffusivity (α) is assumed to be constant for the medium; that is, the medium is assumed to be homogeneous and thermal diffusivity is assumed to be a weak function of temperature to combine Equations (3.1) and (3.2):

$$\left[\frac{1}{r} \frac{d}{dr} \left(r \frac{dT}{dr} \right) \right] = \frac{m}{\alpha} \equiv C \quad (3.3),$$

where C is constant.

This ordinary differential equation is integrated once:

$$r \frac{dT}{dr} = \frac{C}{2} r^2 + I_o \quad (3.4),$$

where I_o is a constant of integration.

Assuming that the heat flux from the heating source is constant, Equation (3.7) is valid at the centerline:

Boundary condition at the centerline:

$$\frac{dT}{dr} = -\frac{q}{k} \approx \omega, \quad \frac{\Delta T}{\Delta t} = \frac{\Delta T}{\Delta t} \bigg|_{r=0_1}, \quad @r = 0 \quad (3.5),$$

where q is the heat flux from the wire, k is the thermal conductivity of the measured medium, and ω is a constant proportional to the heat flux from the heat source at the centerline and thermal conductivity of the measured medium.

When the constant ω is substituted at the centerline boundary ($r = 0$) into Equation (3.4), I_0 is eliminated.

If the temperature is known at some distance (R_1) from the heat source, a boundary condition can be provided at that distance:

Boundary condition written at the radial distance R_1 :

$$T = T_1, \quad \frac{\Delta T}{\Delta t} = \frac{\Delta T}{\Delta t} \bigg|_{r=R_1}, \quad @r = R_1 \quad (3.6).$$

Likewise, if the temperature is known as some other distance (R_2) from the heating line, another condition is known:

Boundary condition similar to Equation (3.6), but at radial distance R_2 :

$$T = T_2, \quad \frac{\Delta T}{\Delta t} = \frac{\Delta T}{\Delta t} \bigg|_{r=R_2}, \quad @r = R_2 \quad (3.7).$$

From boundary conditions Equation (3.6) and Equation (3.7), if the temperature is measured at two known distances from the heat source, integration of Equation (3.4), with I_0 equaling 0, thermal diffusivity, α , can be calculated (recalling that $\alpha = m/C$).

$$T = \frac{C}{4} r^2 + I_1 \quad (3.8)$$

where I_1 is a second constant of integration.

When Equation (3.8) is applied at the first location, boundary condition 2 follows:

$$T_1 = \frac{C|_{r=R_1}}{4} R_1^2 + I_1 \quad (3.9)$$

At the second location, a similar equation follows from boundary condition 3:

$$T_2 = \frac{C|_{r=R_2}}{4} R_2^2 + I_1 \quad (3.10)$$

Elimination of the integrating factor, I_1 , gives the following equation:

$$T_2 - T_1 = \frac{C|_{r=R_2} R_2^2 - C|_{r=R_1} R_1^2}{4} \quad (3.11)$$

From Equations (3.2) and (3.3) we know that $C_i = (\Delta T / \Delta t)_i / \alpha_i$, where i represents the location of the measurement. Substitution into Equation (3.11) for the respective locations, and assumption of constant thermal diffusivity throughout the measured material results in an expression for thermal diffusivity:

$$\alpha = \frac{\left[\frac{\Delta T}{\Delta t}\right]_{r=R_2} R_2^2 - \left[\frac{\Delta T}{\Delta t}\right]_{r=R_1} R_1^2}{4(T_2 - T_1)} \quad (3.12)$$

Equation (3.12) is the final equation used in the experiments; however, it can be seen that as R_1 approaches 0 (the exact center) the second term in the numerator diminishes, further simplifying the equation and experimental procedure since the temperature change with time at the center would no longer be needed.

Although in our experiments the center thermocouple was close to the center, its temperature with time was included in the thermal diffusivity analyses for completeness.

A summary of the assumptions made to achieve Equation (3.12) for thermal diffusivity is as follows:

1. thermal diffusivity does not vary with temperature, time, or distance,
2. the heat source emits a constant energy flux,
3. the measured medium has infinite radius, which does not allow for the heat wave to reach the cylinder wall,
4. the medium is a long cylinder, i.e., no heat transfer in the axial direction, and
5. the change in temperature with time is linear.

4. EXPERIMENTAL PROCEDURE

A medium such as ice, hydrate, or composites with sediment is formed in place around the axial wire in the cell. For ice, deionized water is cooled in the cell until ice forms. For hydrate or hydrate-sediment mixtures, the method introduced by Stern et al. [6], which converts crushed ice into hydrate, can be used.

Initially, no power is supplied to the heating wire. Once the medium for measurement is formed in place, the bath temperature is held constant until all thermocouples have registered identical temperatures. At uniform temperature, power is supplied. As the heat wave moves through the medium, thermocouple temperatures begin to rise. Experiments are conducted until a rise in cell wall temperature indicates the heat wave is at the wall, invalidating assumption 2.

An example of a thermal diffusivity experiment for ice is shown in Fig. 2. The temperature rates were measured by averaging the slope of the temperature over the same interval of time for both thermocouples. The interval of time was chosen for each experiment based on the following criteria:

1. The center and midway thermocouples register an increase in temperature
2. A linear slope was observed in thermocouples at distances R_1 and R_2
3. The wall thermocouple did not register a rise in temperature
4. The center temperature did not exceed hydrate equilibrium

The temperatures T_1 and T_2 were obtained by averaging temperatures over the time interval. The temperature at which the thermal conductivity measurement was taken was estimated by the mean of T_1 and T_2 (that is $(T_1+T_2)/2$).

5. ERROR ESTIMATES

This new method was tested by conducting experiments with ice in the cell. Five thermal diffusivity points were measured at about 271K. The thermal diffusivity values for these experiments ranged between 1.1×10^{-6} and 1.2×10^{-6} as shown in Tab. I.

To compare with literature values for ice, thermal conductivity, k , was calculated from the range values by using ice density, ρ , of 920 kg/m³ and heat capacity, C_p , of 2,040 J/kgK in the definition for thermal diffusivity:

$$\alpha \equiv \frac{k}{\rho C_p} \quad (5.1).$$

Comparison of these values is summarized in Tab. II and shown in Fig. 3. The values from the new technique agree well with those from other sources [7, 8, 9, 10, 11].

The offset error can be cast into Equation (5.2):

$$y_i = \mu_i + \varepsilon_i \quad (5.2),$$

where y is the measured value, μ is the true value, and ε is the offset from the true value for measurement, i .

The thermocouples were calibrated using a thermometer accurate to 0.1K. At constant temperature, each thermocouple registered identical average temperatures (except for noise). Therefore, if all thermocouples had offset error, the errors were identical. For identical offset errors ($\varepsilon_1 = \varepsilon_2$), a difference in measurements helps to eliminate the offset:

$$\Delta y = \Delta \mu \quad (5.3).$$

Since Equation (3.12) utilizes the temperature difference at two locations, and offset in each thermocouple is identical, the errors tend to cancel. Additionally, the offset error is not important when measuring the temperature-time slopes. It should be noted however, that offset error could occur when determining the average temperature of the experiment, as this is not a difference of measurements. After calibration, this error was reduced to $\pm 0.2 \%$, or $\sim 0.5^\circ\text{C}$ at 273K.

Other sources for error could exist from heat loss at the cell wall and melting of the measured medium at the heating element. From the ice experiments, total error is $\pm 5\%$.

The primary alternative method for thermal diffusivity measurements is that of the von Herzen and Maxwell probe [12], which is reported to have error of around $\pm 30\%$ [13]. The experiment described in the current manuscript, with an estimated error of $\pm 5\%$, has significant thermal diffusivity measurement accuracy over the von Herzen and Maxwell probe. The drawback to the current method is that the measured medium must be formed around the heating element and thermocouples, while the von Herzen and Maxwell probe can be inserted into existing media.

The accuracy of the technique can be improved by three experimental modifications:

1. thermocouples with higher accuracy,
2. larger diameter cell to allow for a longer measurement, and
3. good insulation around the cell to prevent loss of heat from the wall.

6. HYDRATE THERMAL DIFFUSIVITY MEASUREMENTS

Thermal diffusivity measurements of pure hydrates were measured using the new thermal diffusivity technique. Hydrates were formed in the cell around the heating wire and thermocouples by first filling the cell with crushed ice from deionized water. The porosity of the hydrate in the cell was controlled between 0.40 \pm 0.42 by sieving the ice particles prior to loading the ice into the cell. Then, the cell was placed into a bath at temperature below the ice point to prevent ice melting. The cell was pressurized above the hydrate equilibrium pressure at the desired experimental temperature with 99.99mol% pure

methane gas, and the temperature in the cell was raised to 274 K. As ice melted, it was converted to hydrate. To ensure complete conversion of ice to hydrate, the temperature was cycled above and below 273.15K until no gas additional was consumed, as indicated by constant pressure.

Pure methane hydrate thermal diffusivities were measured at temperatures ranging between 265.3K and 281.7K. The results of the hydrate thermal diffusivity at various temperatures are tabulated in Tab. III and shown in Fig. 4. As can be seen, hydrate thermal diffusivities remain nearly constant with temperature for the range measured.

7. CONCLUSIONS

A new hydrate thermal diffusivity experiment was constructed. The experiment was verified by measuring thermal diffusivity of a known substance, ice. The error from the experiment appears to be $\pm 5\%$, which is an improvement from the alternative von Herzen and Maxwell technique ($\pm 30\%$). Pure methane hydrate thermal diffusivity for various temperatures has been measured by the new technique. These values ranged from $3.33 \times 10^{-6} \text{ m}^2/\text{s}$ to $3.12 \times 10^{-6} \text{ m}^2/\text{s}$ at temperatures from 265K to 282K, respectively.

ACKNOWLEDGEMENTS

This work was supported by the Center for Hydrate Research Consortium including BP Amoco Exploration, ChevronTexaco, ExxonMobil, Halliburton Energy Services, the Oil and Natural Gas Corporation of India, PhillipsConoco, and Unocal.

REFERENCES

1. K. A. Kvenvolden, *Chemical Geology*, **71**, (1988), pp. 41-51.
2. T. S. Collett, in *Natural Gas Hydrate in Oceanic and Permafrost Environments*, (Kluwer Academic Publishers, the Netherlands, Michael D. Max, Ed., 2000), pp.123-136.
3. M. Kastner, in *Natural Gas Hydrates: Occurrence, Distribution, and Detection*, (American Geophysical Union, Washington D. C., C. K. Paull and W. P. Dillon, Ed., 2001), pp. 67-86.
4. W. F. Waite, B. J. deMartin, J. Pinkston, S. H. Kirby, and C. D. Ruppel, *Geophysical Research Letters*, (2001)
5. H. S. Carslaw and J. C. Jaeger, in *Conduction of Heat in Solids*, 2nd ed. (Oxford University Press, New York, 1959), p17.
6. L. A. Stern, S. H. Kirby, W. B. Durham, S. Circone, and W. F. Waite, in *Natural Gas Hydrate in Oceanic and Permafrost Environments*, (Kluwer Academic Publishers, the Netherlands, Michael D. Max, Ed., 2000), pp. 323-348.
7. V. J. Lunardini, in *Heat Transfer in Cold Climates*, (Van Nostrand Reinhold Company, New York, 1981), pp. 309.
8. W. F. Waite, J. Pinkston, and S. H. Kirby, *Proceedings of the Fourth International Conference on Gas Hydrates*, (Yokohama, Japan, May 19-23, 2002), pp. 728-733.
9. F. P. Incropera and D. P. DeWitt in *Fundamentals of Heat and Mass Transfer*, 4th ed. (John Wiley and Sons, Inc., New York, 1996), p. 838.

10. E. D. Sloan, in *Clathrate Hydrates of Natural Gases*, 2nd ed. (Marcel Decker, Inc., New York, 1998), p 60.
11. J. G. Cook and D. G. Leaist, *Geophysical Research Letters*, **10**, (1983), pp. 397-399.
12. R. P. von Herzen and A. E. Maxwell, *J. of Geophysical Research*, **64**, (1959), pp. 1557-1563.
13. Hukseflux Thermal Sensors, *TP02 Non-steady-state probe for thermal conductivity measurement user manual*, Version 0107, (The Netherlands, 2000), p.39.

Table I. Thermal Diffusivity for Ice.

Experiment No.	Temperature (K)	Thermal diffusivity, α ($\text{m}^2/\text{s} \times 10^6$)
1	270	1.2
2	271	1.1
3	271	1.1
4	271	1.2
5	271	1.2
average	271	1.2

Table II. Comparison of Thermal Conductivity Values for Ice from Various Sources.

Source	Temperature (K)	Thermal conductivity, k (W/mK)
Lunardini, 1981	233	2.66
Waite et al., 2002	253	~2.12 ^a
Incropera and DeWitt, 1996	253	2.03
Sloan, 1998	263	2.23
Waite et al., 2002	263	~2.01 ^a
Cook and Leaist, 1983	268	2.19
This work	271	2.18 ^b
Lunardini, 1981	273	2.21
Incropera and DeWitt, 1996	273	1.88

^aValues are estimated from points on a figure

^bCalculated from measured thermal diffusivity data, assuming density = 920 kg/m³ and C_p = 2,040 J/kgK [9].

Table III. Thermal Diffusivity of Pure Methane Hydrate at Various Temperatures

Temperature (K)	Pressure (MPa)	Thermal diffusivity, α ($\text{m}^2/\text{s} \times 10^7$)
265	4.34	3.33 ± 0.17
266	4.34	3.34 ± 0.17
269	4.38	3.24 ± 0.16
274	4.38	3.17 ± 0.16
282	6.79	3.12 ± 0.16

Figure Captions

Fig. 1. Thermal diffusivity apparatus.

Fig 2. Example of a thermal diffusivity experiment for ice.

Fig. 3. Comparison of ice thermal conductivity with temperature from various sources.

Fig. 4. Thermal conductivity of pure methane hydrate with temperature.

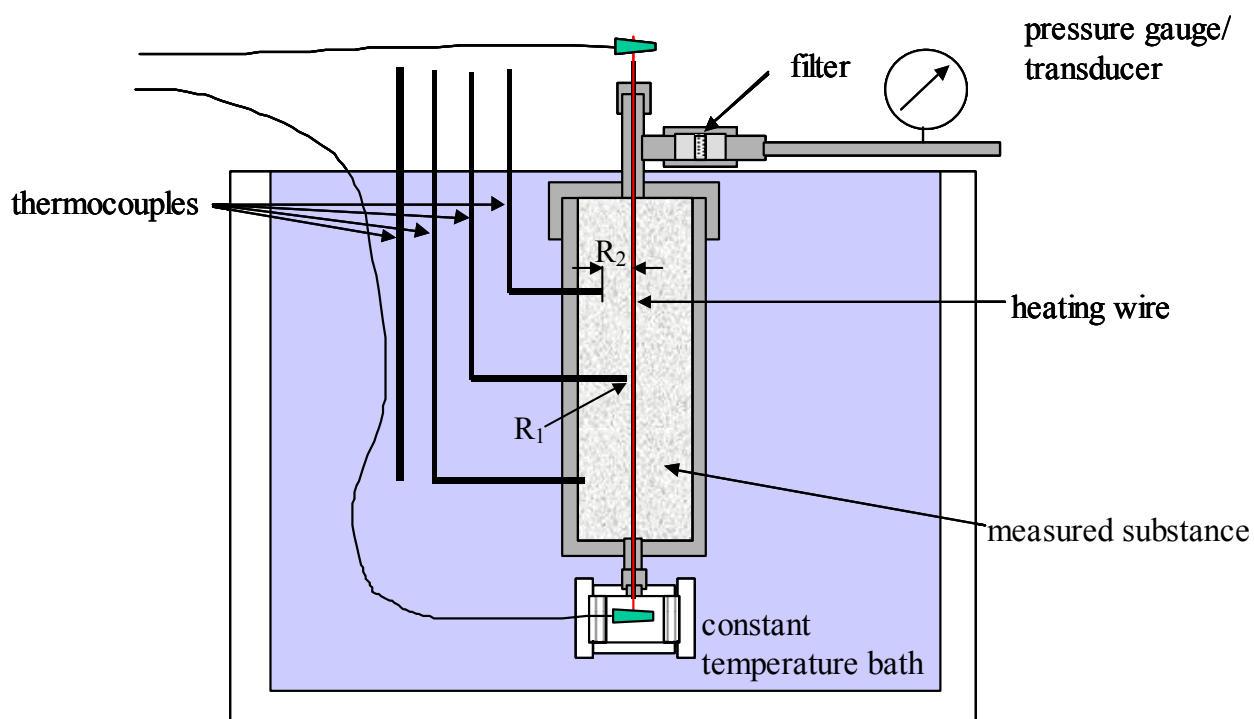


Fig. 1

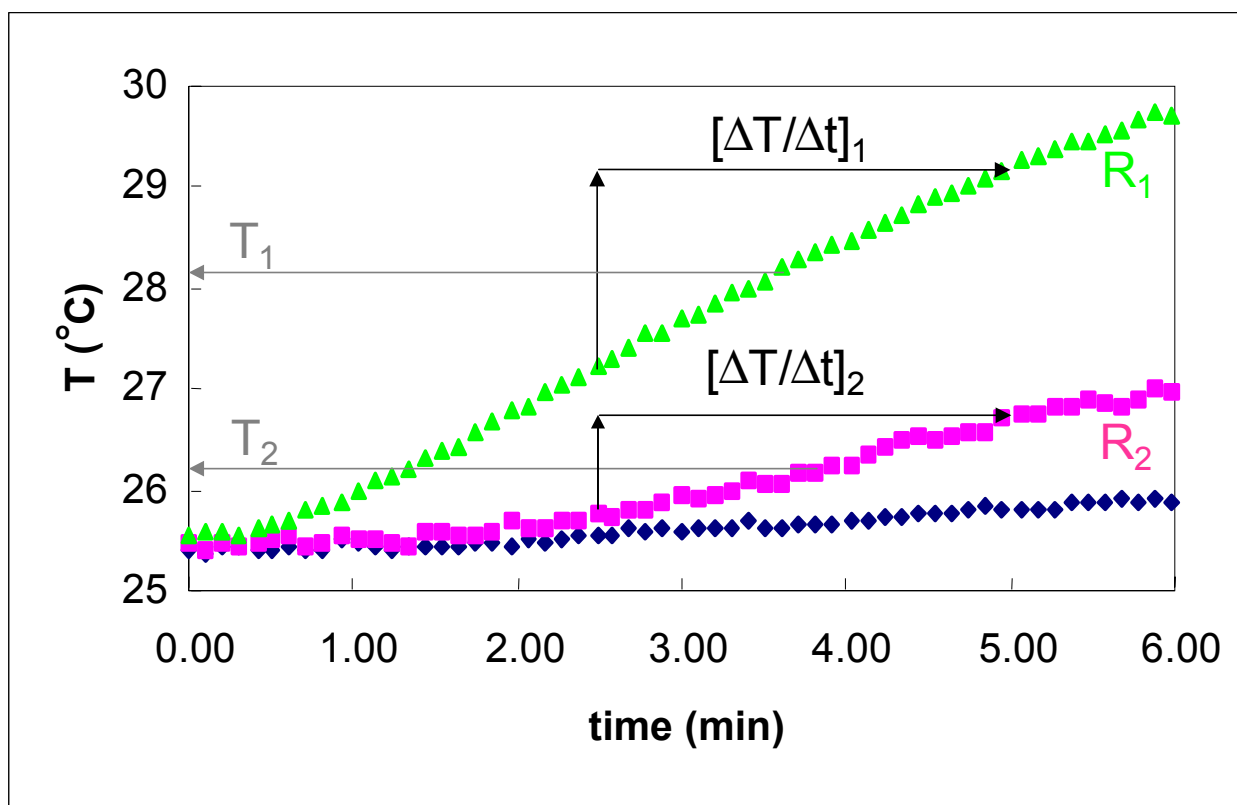


Fig. 2

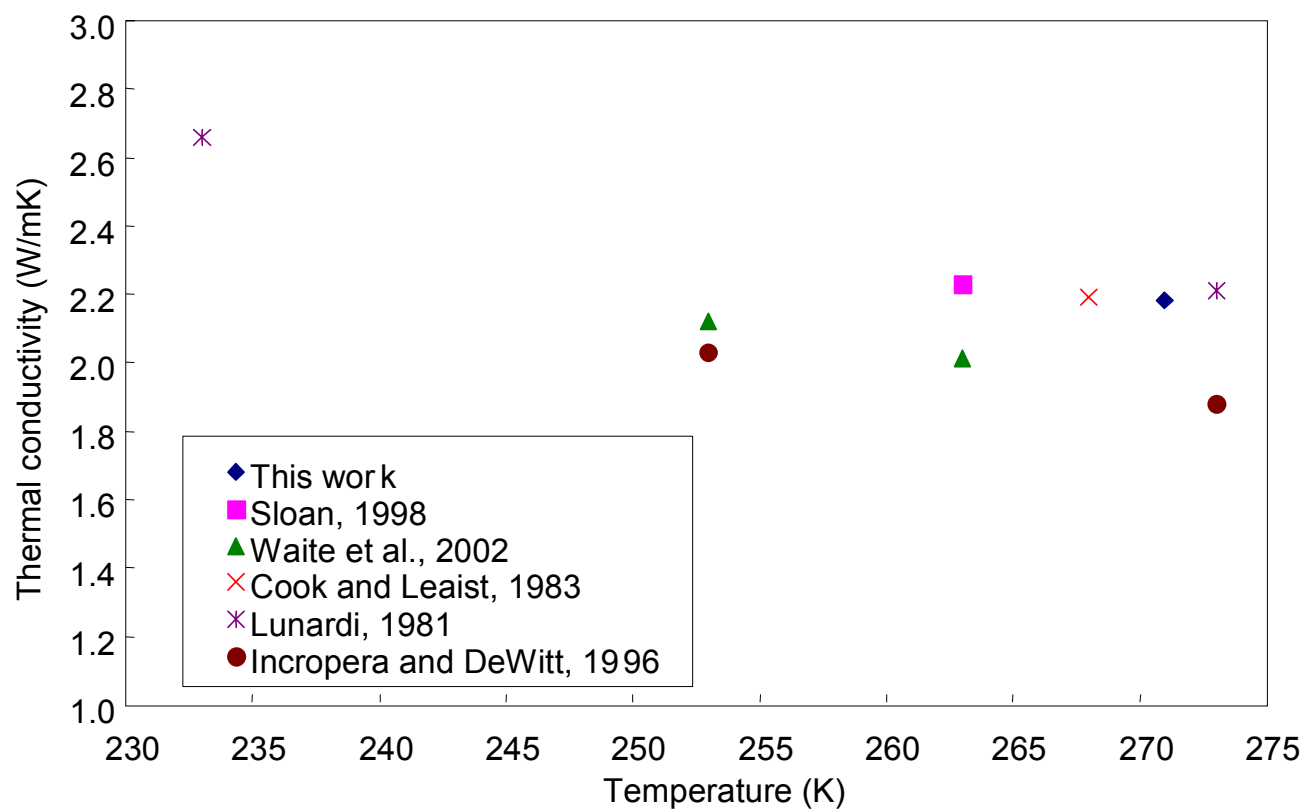


Fig. 3

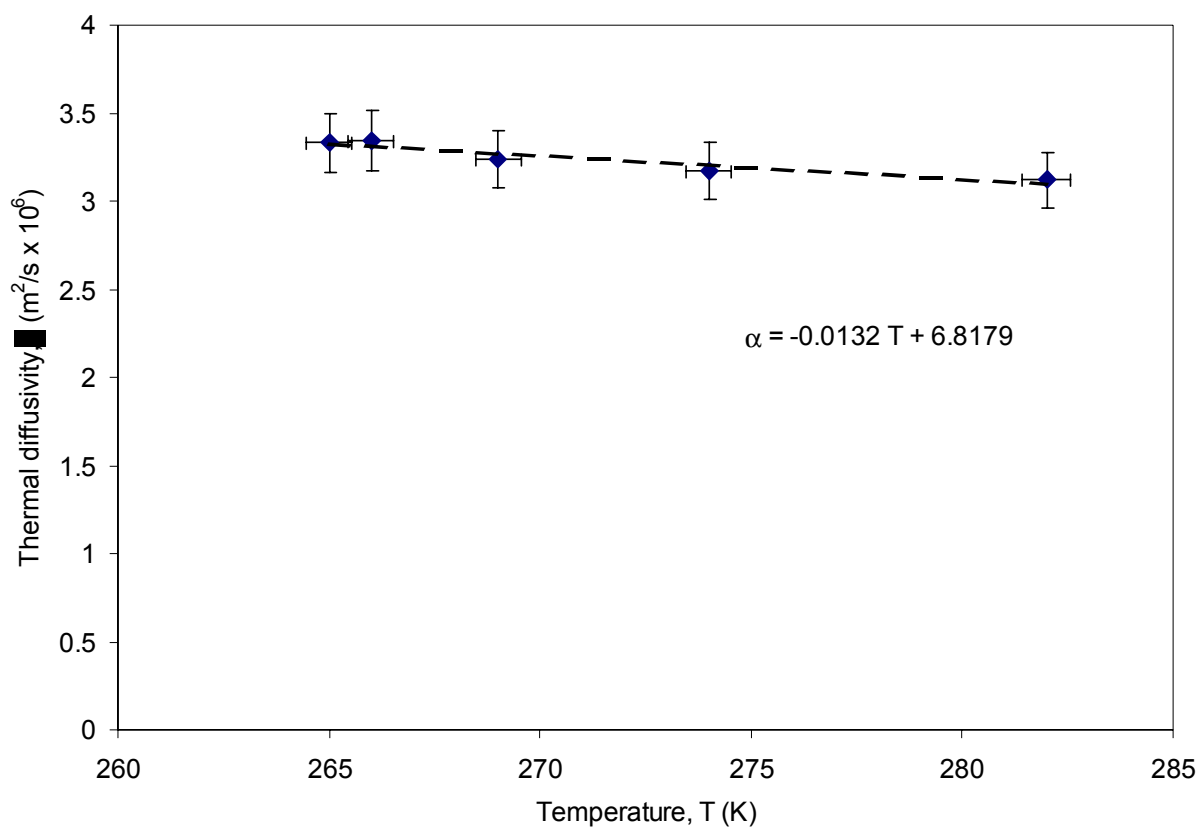


Fig. 4